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AFRPL-TR-66-131

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# **(U) HIGH RESOLUTION MASS SPECTROGRAPHIC INVESTIGATION OF PROPELLANT PROCESSES**

**BERGE B. GOSHGARIAN**

**TECHNICAL REPORT AFRPL-TR-66-131**

**JUNE 1966**

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HIGH RESOLUTION MASS SPECTROGRAPHIC  
INVESTIGATION OF PROPELLANT PROCESSES (U)

Berge B. Goshgarian

Technical Report AFRPL-TR-66-131

June 1966

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## FOREWORD

(U) The effort described in this report was performed under task 314802802, "High Resolution Mass Spectrographic Investigation of Propellant Processes." It was one phase of in-house project 314802002, entitled "Exploratory Propellant Research", which was a broad effort encompassing several tasks on exploration of advanced propellant synthesis and evaluation techniques. This is the final report under task 314802802.

This report has been reviewed and approved.



ELWOOD M. DOUTHETT

Colonel, USAF

Commander, Air Force Rocket Propulsion Laboratory

# UNCLASSIFIED ABSTRACT

Propellants and their combustion products were studied with a multisource high-resolution mass spectrometer. A spark ion source, gas ion source, and Knudsen effusion cell were used to study solid, liquid, and gaseous samples. Techniques were developed to study contaminants in propellants as well as the handling of corrosive oxidizers. The results of studies of propellant ingredients, corrosive oxidizers, and combustion products given show that the multisource mass spectrometer, with special propellant handling techniques, is a useful tool for the study of propellant characterization and combustion products.



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## SECTION I

### (U) INTRODUCTION

The use of mass spectrometry for data acquisition in propellant research has been increasing. The versatility of this analytical tool has provided propellant chemists and engineers with much needed data on propellant and propellant contamination identification, thermodynamic values, and propellant kinetics. Primary emphasis of this task was to obtain such data in support of propellant evaluation programs being conducted at the Air Force Rocket Propulsion Laboratory.

The mass spectrometric methods utilized included the vacuum spark ion source, the Knudsen effusion cell, and the gas ion source.

The spark ion source has been used primarily to analyze metals and semi-conductors for trace contaminants (1, 2, 3, 4). Some studies have been conducted with powder matrices of geological specimens and insulating powders (1, 4). No studies on propellants or propellant combustion products have been reported previously. Consequently, this phase of the task was undertaken to provide a useful means of identification of major and minor ingredients in solid propellants and propellant combustion products.

The Knudsen effusion technique in combination with a mass spectrometer has been used to acquire thermodynamic data on propellant products (5, 6). The needed thermodynamic data for some propellant combustion products was either in doubt or not readily available. Application of this technique was investigated to see whether information could be obtained which would fill in voids in thermodynamic data or add to existing information for a more thorough understanding of thermodynamic processes in propellant combustion.

Applicability of mass spectrometric methods for research corrosive oxidizers has been limited in the past by the reactivity of the oxidizers and the instrument hardware. In this effort, gas ion source techniques have been successfully applied to acquire data on corrosive oxidizers.

## SECTION II

### (U) EXPERIMENTAL PROCEDURE

The basic instrument used was a Mattauch-Herzog geometry double-focusing mass spectrometer built by the Consolidated Electrodynamic Corporation. Resolution attainable with this geometry was 0.001 mass units with a mass range from 1 to 5000. Photographic plates were required for the spark method because of the erratic nature of ion production during sparking of a sample. Integration of ion species during a time lapse on the photo plate reduced the probability of inaccurate data collection because of unstable ion production.

The electron-multiplier and electrometer were used for analysis of gases effusing from a high-temperature Knudsen cell, as well as for gases introduced directly to the mass spectrometer ion source. Since gas ion source techniques afford more stable ion production, data can be collected electrically and produced on a recorder trace.

Two separate sources for ion production were used: a vacuum spark ion source and a gas ion source. The former utilized an 80 to 100 kv radio-frequency spark, adjustable from 10 to 1000 pulses per second, to ionize solid samples. Solid samples could be handled either as "chunks" or powders. The "chunks" were clamped into holders in the source which are adjustable from outside the vacuum chamber to permit alignment with the slit system in the instrument. Powder samples were packed into cupped pure silver electrodes and loaded into the holders as previously described. Samples were probed during analysis using a needle-tipped rod made from the sample or cupped electrode material.

The gas ion source consisted of a rhenium filament for the electron bombardment source and related ion optics. This source was used for gas

analysis, including identification and appearance potential measurements. The gas introduced into the ion source either originated from the Knudsen effusion cell or was introduced through a gas handling system built onto the source housing.

Three methods were used for analysis of solid, liquid, and gaseous propellants. The spark ion source previously discussed was used to analyze solid propellants and propellant combustion products for contaminants and major constituents.

The Knudsen effusion cell, capable of reaching a temperature of  $2400^{\circ}\text{K}$ , was used to obtain thermodynamic data on solid propellants and solid combustion products. Samples were loaded into a crucible and placed in the Knudsen cell housing, evacuated, and heated. Gases evolved from the sample were ionized in the gas ion source, and the ions were detected by means of the electrical detection system described.

A special Monel gas-liquid handling system was added to the gas source housing for introduction of corrosive liquid and gaseous propellants. The glass system originally delivered with the instrument could not be used because of the corrosive nature of the propellants investigated.

### SECTION III

#### (U) RESULTS AND DISCUSSION

##### (U) A. SPARK SOURCE STUDIES

###### (U) 1. Engine Combustion Products.

The first propellant combustion products investigated with the spark ion source were those from pentaborane-hydrazine tests. Combustion efficiency was lower than expected, and incomplete combustion of the propellants with consequent formation of undesirable products was suspected.

Samples of solid combustion products were collected and subjected to 1-micron vacuum and 180° centigrade temperature to remove trapped gases. The powder sample was then packed into cupped silver electrodes for analysis.

Ion species originating from the sample during spark analysis were collected on a pressure-sensitive photoplate and qualitatively identified. Species observed included boron, carbon, nitrogen, oxygen, and other less concentrated ions, as shown in Table I. Other molecular species observed included BH, NH, and BNH types. The desired reaction products in the combustion chamber were boron nitride and hydrogen; however, lowered combustion efficiency was suspected because of incomplete reaction. Good correlation was obtained between combustion efficiency and the concentration of the BH-NH-BNH type of ion species in the sample analysis. Whenever efficiency was high, these species were low, and vice versa. This correlation was observed both with combustion product samples from the Air Force Rocket Propulsion Laboratory and contractor firings.

(U) TABLE I

COMPUTED MASS VERSUS TRUE MASS OF IDENTIFIED  
MASS FRAGMENTS IN COMBUSTION PRODUCTS

Mass (Computed)	Mass (True, $^{12}\text{C} = 12.0000$ )	Combustion Product Mass (Fragment)
10.0163	10.0129	$^{10}\text{B}$
11.0160	11.0093	$^{11}\text{B}$
12.0011	12.0000	$^{12}\text{C}$
12.0173	12.0171	$^{11}\text{BH}$
13.0046	13.0078	$^{12}\text{CH}$
13.0244	13.0249	$^{11}\text{BH}_2$
14.0110	14.0141	$^{12}\text{CH}_2$
14.0001	14.0031	$^{14}\text{N}$
15.0015	15.0001	$^{15}\text{N}$
15.0143	15.0109	$^{14}\text{NH}$
15.9991	15.9950	$^{16}\text{O}$
16.0173	16.0187	$^{14}\text{NH}_2$
17.0057	17.0027	$\text{OH}$
17.0283	17.0265	$^{14}\text{NH}_2$
18.0138	18.0106	$\text{HOH}$
18.0354	18.0313	$^{14}\text{NH}_4$
19.0037	18.9984	$^{19}\text{F}$
22.9896	22.9898	$^{23}\text{Na}$
23.9859	23.9850	$^{24}\text{Mg}$
25.0101	25.0123	$^{11}\text{B}^{14}\text{N}$
26.0104	26.0078	$^{10}\text{BO}$

(U) TABLE I (Cont'd)

COMPUTED MASS VERSUS TRUE MASS OF IDENTIFIED  
MASS FRAGMENTS IN COMBUSTION PRODUCTS

Mass (Computed)	Mass (True, $^{12}\text{C} = 12.0000$ )	Combustion Product Mass (Fragment)
26.9861	26.9815	$^{27}\text{Al}$
27.0089	27.0042	$^{11}\text{BO}$
27.9770	27.9769	$^{28}\text{Si}$
28.0060	28.0062	$^{14}\text{N}_2$
29.0123	29.0139	$^{14}\text{N}_2\text{H}$
31.9752	31.9721	$^{32}\text{S}$
34.9669	34.9688	$^{35}\text{Cl}$
35.0196	35.0253	$^{10}\text{B}^{11}\text{B}^{14}\text{N}$
36.0188	36.0217	$^{11}\text{B}_2^{14}\text{N}$
36.9657	36.9659	$^{37}\text{Cl}$
39.9696	39.9626	$^{40}\text{Ca}$
89.9093	89.9043	$^{90}\text{Zr}$

## (U) 2. Quantitative Analysis.

Quantitative identification of constituents in solids using the spark ion source was difficult. Sensitivities of elements and molecules to ion formation in the spark source were known to vary by as much as a factor of six. Consequently, known concentration standards had to be spark-analyzed and the sensitivities of the elements in the solid matrix determined. The resultant sensitivity values were then used to calculate quantitative data for these elements present in other solid matrices. This method provided quantitative data, but involved a considerable

amount of time. A method was desired to calculate sensitivities for any element or molecule suspected in a sample without first spark-analyzing standards.

All previously derived sensitivities were thoroughly investigated. The physical and chemical nature of the elements was also investigated as to its contribution to the large sensitivity change among elements. The results indicated that cross-sectional area of the elemental atom, heat of vaporization, ionization potential, and molecular weight contributed significantly to the sensitivity of an element in the spark ion source.

Calculated sensitivities for some elements, using the above parameter obtained from the published literature, are presented in Table II. The equation used to calculate these sensitivities is given below:

$$S_m = (CA) \times \frac{1}{H_{\text{vap}}} \times \frac{1}{I_p^+} \times \sqrt{\frac{1}{M}}$$

Where

$S_m$  = Sensitivity of element with molecular weight  $M$ .

$CA$  = Cross-sectional area.

$\bar{\Delta}H_{\text{vap}}$  = Heat of vaporization.

$I_p^+$  = First ionization potential.

$M$  = Elemental molecular weight.

Analysis of standard samples was conducted and the above calculated sensitivities applied to the quantitative analysis to check the accuracy of the calculation method.



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(U) TABLE II

## CALCULATED ELEMENTAL SENSITIVITIES

Element	Sensitivity x 10 <sup>2</sup>
Li	6.1
Be	0.84
B	0.39
C	0.21
Na	6.2
Mg	3.2
Al	1.5
Si	0.67
P	0.78
K	16.0
Ca	3.8
Ti	0.74
V	0.73
Cr	0.80
Mn	0.85
Fe	0.55
Co	0.51
Ni	0.56
Cu	0.60
Zn	1.5
Rb	13.5
Zr	0.50
Mo	0.36
Ag	0.76
Cs	15.0
W	0.19

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Table III shows analytical data for an NBS Hastalloy C standard sample. In most instances, when the calculated sensitivities were not used, results were far from accurate. Use of the calculated sensitivity values gave results comparable to the NBS standard data.

(U) TABLE III  
HASTALLOY C ANALYSIS

Element	Uncorrected Weight %	Corrected Weight %	NBS Weight %
C	.13	.30	.06
Si	.61	.49	.51
V	.35	.25	.2
Cr	23.9	16.5	15.7
Mn	1.7	1.0	.6
Fe	6.3	6.1	5.7
Ni	51.0	48.4	52.6
Co	1.5	1.6	1.4
Mo	13.3	18.5	16.5
W	2.9	6.9	3.4

(C) (U) 3. Propellant Ingredient Studies.

(C) Samples of aluminum and beryllium hydrides were obtained from the manufacturers for analysis. The aluminum hydride samples were analyzed by wet-chemical techniques, and subjected to spark ion source analysis. Application of the calculated sensitivities to the spark data gave results comparable to the wet chemical analysis, as shown in Table IV. The lithium and boron in the samples originated from the lithium borohydride added during the preparation of aluminum hydride. Magnesium and sodium probably come from the respective chlorides in one of the starting materials, aluminum chloride. No other elements, other than carbon and oxygen from solvents, were detected. The minimum level of detection for this series of analysis was 10 ppm.

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(C) TABLE IV  
ALUMINUM HYDRIDE ANALYSIS  
DOW 1451

Ele - ment	Sample 1		Sample 2		Sample 3	
	Wet Chemical	Spark Source	Wet Chemical	Spark Source	Wet Chemical	Spark Source
Li	.37	.2	.3	.2	.51	.5
B	--	.02	--	.01	Under 0.1	.04
C	.12	.3	.39	.3	.3	.6
O	--	.35	--	.6	--	.8
Na	--	.03	--	.05	--	.05
Mg	--	.04	--	.12	--	.08
Al	98.3	99.0	98.8	98.8	98.0	98.2
Cl	Under 0.1	.02	.33	.10	Under 0.1	.04
Un- known	1.10	--	--	--	--	--

(C) The spark ion source method was also used for quantitative and qualitative identification of constituents in beryllium hydride. Table V shows the ion species found in the spark analysis of beryllium hydride sample PP142-143. The average ion intensities are computed from actual ion line intensities on the photoplate, and are not corrected for sensitivity. Species corresponding to organo-beryllium compounds in the sample were easily detected. Other species detected, but not included in the table, were sodium, magnesium, aluminum, phosphorous, sulfur and chlorine.

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(C) TABLE V  
BERYLLIUM HYDRIDE ANALYSIS

Ion	Average Intensity
Be	100.0
BeH	10.0
C	50.0
CH	7.8
CH <sub>2</sub>	1.8
CH <sub>3</sub>	1.4
O	3.8
OH	1.0
Be <sub>2</sub>	.15
F	.02
Be <sub>2</sub> H	.07
Be <sub>2</sub> H <sub>2</sub>	.02
BeC	.02
Be <sub>2</sub> H <sub>3</sub>	.03
BeCH	.02
BeCH <sub>2</sub>	.04
BeCH <sub>3</sub>	.06
BeC <sub>2</sub> H	.04
BeC <sub>2</sub> H <sub>2</sub>	.03
BeC <sub>2</sub> H <sub>3</sub>	.02
BeC <sub>2</sub> H <sub>4</sub>	.01

(C) Impurity ion intensities for samples K71-72, B74-75, and PP142-143 are given in Table VI. One notes that differences in ion intensities are easily distinguishable with respect to sample purity. The low purity for K71-72 (80%) can be attributed to increased quantities of hydrocarbons, oxides, sodium chloride and aluminum. The difference in purity between B74-75 (96%) and PP142-143 (92%) appears to be oxides and hydroxides.

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(C) TABLE VI

## BERYLLIUM HYDRIDE IMPURITY ANALYSIS

Ion	K71-72	B74-75	PP142-143
	80% Pure	95% Pure	92% Pure
CH	1.00	1.00	1.00
CH <sub>2</sub>	.55	.26	.24
CH <sub>3</sub>	.77	.29	.20
O	5.1	.18	.98
CH <sub>4</sub>	.17	.04	.03
OH	.86	.03	.22
HOH	1.28	.03	.06
Na	7.9	.11	.03
C <sub>2</sub>	.12	.09	--
C <sub>2</sub> H	.17	.14	.01
C <sub>2</sub> H <sub>2</sub>	.63	.47	.03
Al	1.8	.03	.02
C <sub>2</sub> H <sub>3</sub>	.51	.21	.04
CO	.30	.02	.01
C <sub>2</sub> H <sub>4</sub>	.49	.10	.02
COH	.14	.01	--
C <sub>2</sub> H <sub>5</sub>	.15	.05	.01
C <sub>3</sub>	.23	.04	.02
C <sub>3</sub> H <sub>2</sub>	.08	.04	--

(C) Quantitative data were obtained on samples which were compressed under high pressure into pellets. This data, given in Table VII, shows that beryllium hydride decomposed under pressure since the ratio of BeH ion to Be ion was lower for the pressed samples, indicating loss of hydrogen.

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(C) TABLE VII  
BERYLLIUM HYDRIDE QUANTITATIVE ANALYSIS

Ion	P142-143 92% Pure	P142-143 Black Solids	B-104 93% Pure
Be	83.0	81.5	83.0
BeH	10.7	4.5	9.2
C	4.9	8.5	4.6
O	1.4	5.5	2.6
Na	--	--	0.2
Cl	--	--	0.4
-----			
Ion	B74-75 Pellet (originally 96% Pure)	K71-72 (80% Pure)	K71-72 Pellet (55% Pure)
Be	44.2	68.3	69.0
BeH	6.5	7.6	3.8
C	46.5	9.9	15.0
O	2.2	7.6	7.3
Na	0.4	5.0	2.9
Cl	0.2	1.8	2.0

(C) The black solids shown in Table VI data were physically picked from PP142-143 samples. This material is primarily beryllium, carbon, and oxygen.

(C) The difference in 80% pure versus 92-93% pure beryllium hydride can be attributable to carbon and oxygen containing compounds as impurities. The large quantity of sodium in K71-72 was attributed to sodium chloride in the sample, which was also found by X-ray techniques (7).

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## (U) 4. Other Studies.

The spark ion source technique has also been applied to the identification of impurities in ammonium perchlorate, propellant binders, materials of construction, and in the qualitative identification of unknown powders and solid materials in rocket engines and propellant systems.

## (U) B. KNUDSEN EFFUSION CELL STUDIES.

### 1. Calibration.

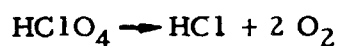
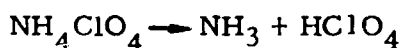
Initial calibration of the Knudsen cell-mass spectrometer system was conducted to determine the accuracy obtainable for thermodynamic data. Results on heat of vaporization determinations for zinc, silver, gold, and aluminum showed that the system was capable of  $\pm 7\%$  accuracy in heat of vaporization determinations, using the slope method where the log of the product of ion intensity and absolute crucible temperature is plotted against inverse crucible temperature in degrees Kelvin.

### 2. Ammonium Perchlorate.

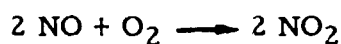
The first propellant sample investigated using this technique was ammonium perchlorate. Initial studies were conducted with the ammonium perchlorate as received. Upon heating in the evacuated Knudsen cell chamber, decomposition was detected at  $100^{\circ}\text{C}$  with liberation of ammonia, water, oxides of nitrogen, oxygen and hydrogen chloride in nonreproducible ratios. Pressure in the cell rose rapidly during the initial heating phase. The crucible temperature was continually raised until reproducible pressure could be obtained. The system was then cooled, and the ammonium perchlorate-containing crucible removed from the cell and weighed. Approximately 30% of the original sample had decomposed. This was also observed by Bircumshaw and Newman (8), who state that decomposition of irregular crystalline forms contributes to the initial thermal decomposition. Further studies were conducted with heat-treated ammonium perchlorate remaining after a  $200^{\circ}\text{C}$  thermal decomposition step.

Three separate activation energy steps of 22.2 Kcal/mole, 29.9 Kcal/mole and 44.0 Kcal/mole were found, as shown in Figure 1. Each step could be attributed to the reactions shown below:

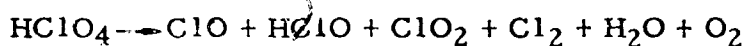
Step I (22.2 Kcal/mole)



Step II (29.9 Kcal/mole)



Step III (44.0 Kcal/mole)



The initial rate-controlling mechanism is the dissociation of ammonium perchlorate into ammonia and perchloric acid. The perchloric acid then undergoes thermal decomposition into hydrogen chloride and oxygen. The oxygen then undergoes reaction with ammonia to give the products corresponding to Step II. Step III appears to involve the dissociation of perchloric acid in the crucible, or fragmentation under electron bombardment in the mass spectrometer ion source.

An activation energy of 29.5 Kcal/mole for the thermal decomposition of ammonium perchlorate was obtained from the slope of a plot of the log cell pressure versus inverse absolute crucible temperature. The cell pressure ranged from  $2 \times 10^{-7}$  torr at 418°K to  $1.2 \times 10^{-5}$  torr at 525°K. An average activation energy, obtained from the slopes of the ion intensities, is  $32.0 \pm 1.6$  Kcal/mole and agrees reasonably well with the pressure-temperature activation energy. Bircumshaw and Phillips (9) reported an activation energy for ammonium perchlorate thermal decomposition of 29.5 Kcal/mole, which agrees with the results obtained in this study.



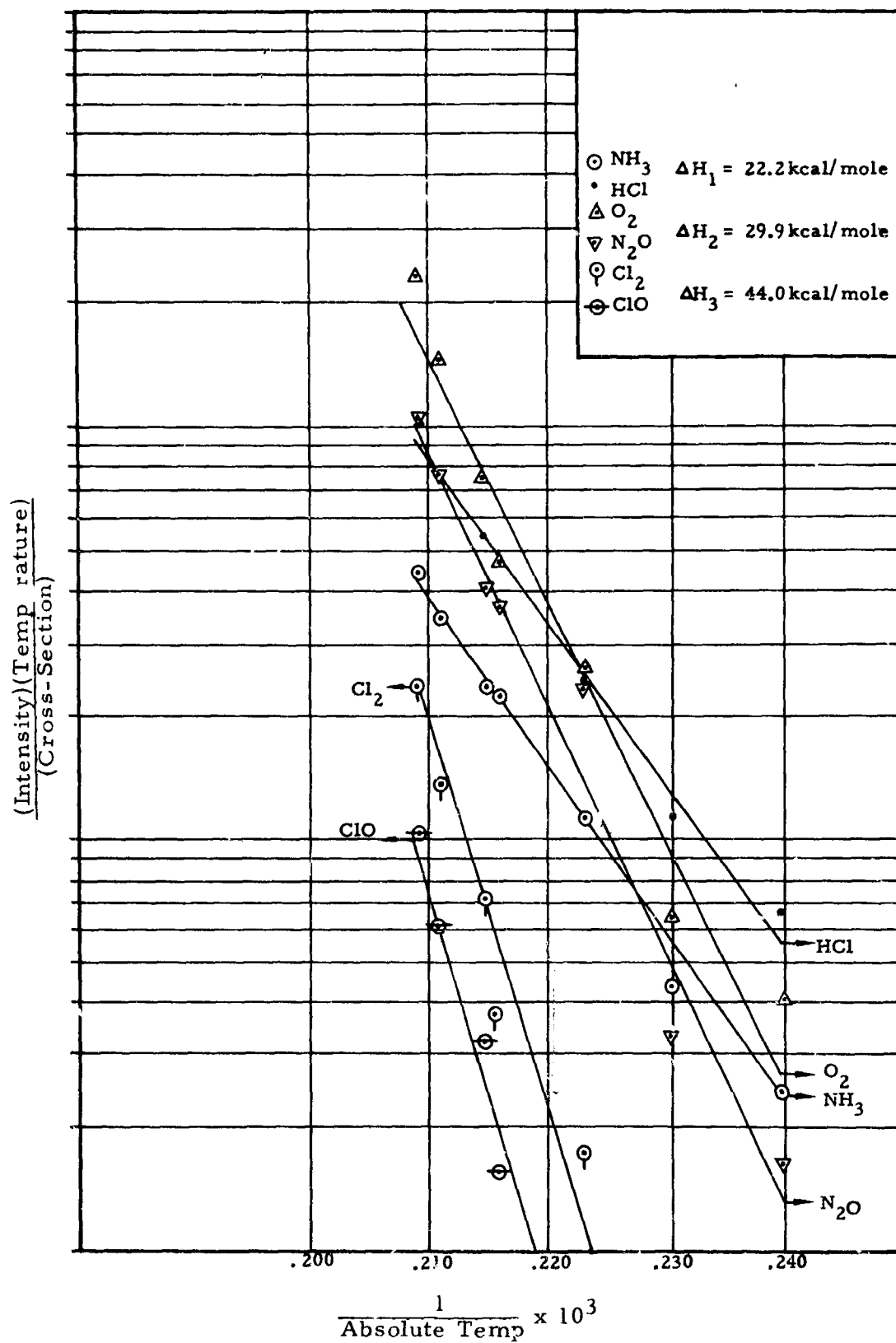


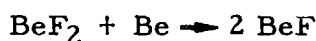
Figure 1. Three Identified Energy Slopes for Ammonium Perchlorate Decomposition

### 3. Beryllium Compounds.

Beryllium nitride, a probable product in rocket engine combustion of propellants containing beryllium and nitrogen, was investigated using this technique. Results obtained showed that beryllium nitride, when heated, decomposed to the elements, with no molecular species existing in the gas phase. The average heat of formation obtained for beryllium nitride, using the slope method, was  $-136 \pm 10$  Kcal/mole. The slopes for two separate runs are shown in Figure 2.

The slope method for calculating heats of formation from Knudsen cell-mass spectrometer data of ion intensities is not very accurate, although most values fall within the range of published (10) data.

The increased use of beryllium-containing propellants required that further thermodynamic data on beryllium-containing solid combustion products be available. The compounds studied next were beryllium monofluoride and difluoride. Due to their high vapor pressure at the investigation temperatures, it was desirable to study these compounds as they were formed in a reaction in the Knudsen cell crucible. The reaction attempted was



The crucible was loaded with calcium fluoride, beryllium, and beryllium oxide. The beryllium oxide was included with the hope that beryllium oxyfluorides could be investigated simultaneously by the following reaction.



Some data on beryllium difluoride was obtained, but was not sufficient for useful thermodynamic data acquisition. As the temperature was raised to initiate beryllium monofluoride formation, the concentration of effusion gases from the crucible rapidly increased. The increased concentration of ionized gases around the crucible caused an uncontrollable rapid rise in the crucible temperature, because of electron transfer from the heated filament used to heat the crucible by electron bombardment, to

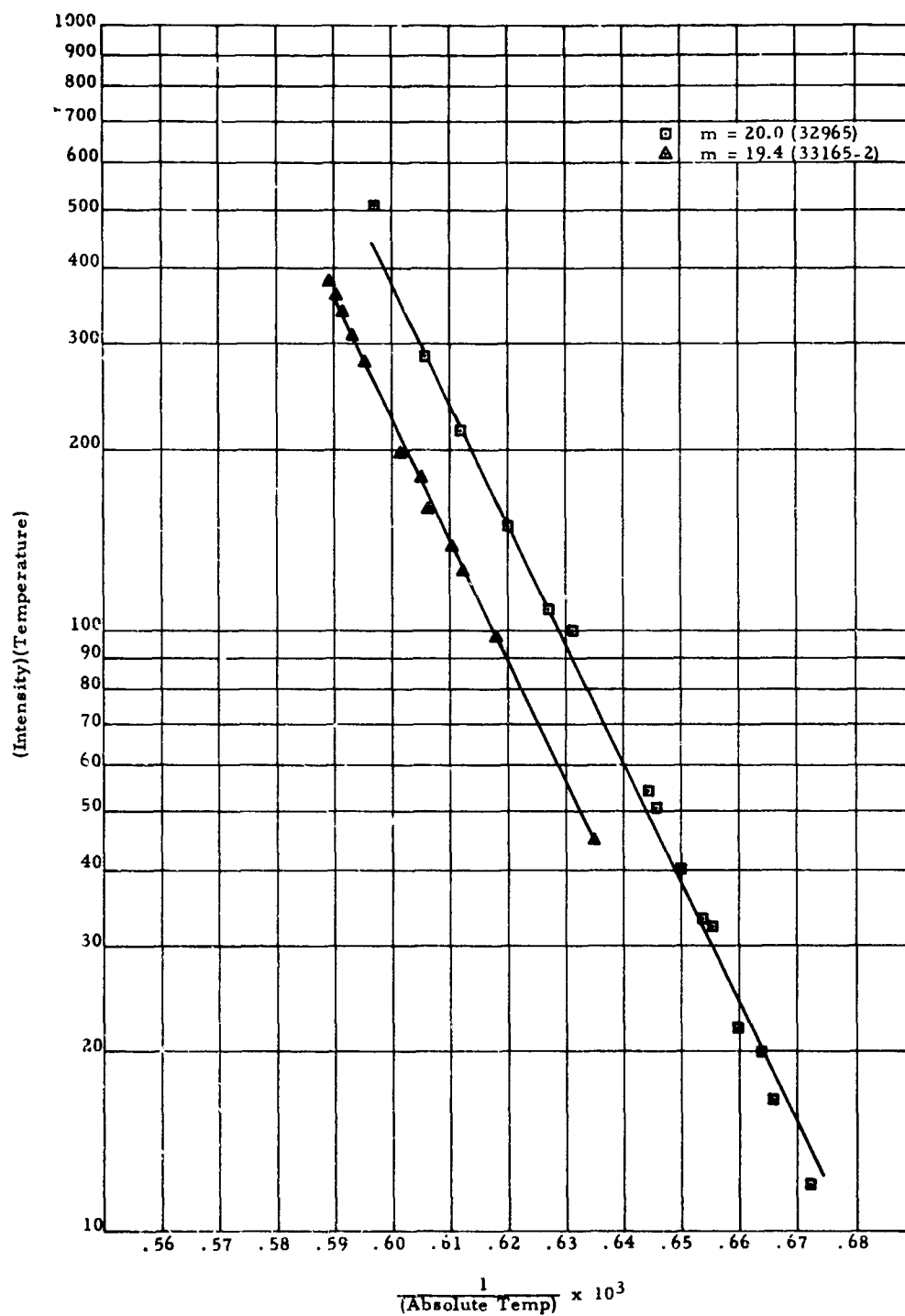


Figure 2.  $\text{Be}^9$  Intensity Slopes, Beryllium Nitride

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the positive potential crucible. The crucible, supports, and other material close to the crucible became very hot and a number of them melted. This investigation was then terminated.

The results showed that modification of the Knudsen cell housing was required to provide increased pumping efficiency and to remove excessive effusing gases. This modification will be used in further Knudsen effusion studies. The manufacturer of the Knudsen effusion cell was notified of this problem; future cells will be modified.

### (C) (U) Gas Source Studies.

(U) The Monel manifold described earlier was initially passivated with the oxidizer to be studied for 12 hours prior to a run. Analysis of the gases sampled before and after passivation in the manifold during a fluorine gas analysis is shown in Table VIII. One notes that after 12 hours very little reaction occurs in the manifold. This technique could be used to study the degree and rate of passivation of materials with corrosive oxidizers.

(U) TABLE VIII  
PRE- AND POST-PASSIVATION ANALYSIS

Ion	Pre-Passivation Intensity	Post-Passivation Intensity
H <sub>2</sub> O	7.9	0.4
HF	1.4	.14
Si	1.81	.08
O <sub>2</sub>	.63	.07
CO <sub>2</sub>	10.9	.03
F <sub>2</sub>	1.00	1.00
SiF <sub>3</sub>	.81	.02

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(C) Samples studied with this system included chlorine pentafluoride, bromine pentafluoride, iodine pentafluoride, fluorine, oxygen difluoride, xenon tetrafluoride, xenon hexafluoride, and two special oxidizer samples for Aerojet Nucleonics. The high resolving power of this instrument proved necessary for these studies. All contaminant peaks were resolved from the major constituent peaks and identified. Also, the use of an all-Monel system and unheated ion source effectively eliminated oxidizer reaction and degradation. This was observed from the stable spectra obtained for highly reactive xenon tetra- and hexafluoride, and the absence of appreciable quantities of reaction products, like silicon tetrafluoride, which form from reactions with the inlet manifold or heated ion source.

(U) Reproducible detection of contaminant hydrogen fluoride, hydrogen chloride, chlorine, silicon tetrafluoride, hydrogen bromide, bromine, oxyfluorides of xenon, and others was obtained with little difficulty. Three spectra each for chlorine pentafluoride and bromine pentafluoride are given in Table IX. Impurities, hydrogen fluoride, hydrogen chloride, organofluoride, silicon tetrafluoride, hydrogen bromide, chloro-bromide, and bromine are shown. Since the manifold was passivated with the sample prior to an analysis, and the spectra for new samples of the same oxidizer were reproducible, the impurities detected must be in the sample and not formed during analysis.

(U) The experience derived from this investigation is being incorporated in the construction of a special oxidizer mass spectrometer for the Air Force Rocket Propulsion Laboratory.

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(C) TABLE IX

## SPECTRA FOR CHLORINE PENTAFLUORIDE AND BROMINE PENTAFLUORIDE

Ion	Relative Intensity	Relative Intensity	Relative Intensity
HF	13	24	19
HCl <sup>35</sup>	4	4	5
Cl <sup>35</sup> F	29	32	30
CF <sub>3</sub>	5	6	3
Cl <sub>2</sub> <sup>35</sup>	7	6	5
Cl <sup>35</sup> F <sub>2</sub>	<u>100</u>	<u>100</u>	<u>100</u>
SiF <sub>3</sub>	4	4	5
Cl <sup>35</sup> F <sub>3</sub>	23	25	21
Cl <sup>35</sup> F <sub>4</sub>	100	103	98
Cl <sup>35</sup> F <sub>5</sub>	0	0	0
HB <sup>79</sup> r	2.2	1.2	1.9
SiF <sub>3</sub>	5.5	5.3	7.1
Br <sup>79</sup> F	29.4	29.7	33.3
Br <sup>79</sup> Cl <sup>35</sup>	3.9	2.8	2.8
Br <sup>79</sup> F <sub>2</sub>	32.9	28.5	29.4
Br <sup>79</sup> F <sub>3</sub>	25.9	26.7	23.9
Br <sup>79</sup> F <sub>4</sub>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Br <sup>79</sup> Br <sup>81</sup>	20.8	18.2	18.3
Br <sup>79</sup> F <sub>5</sub>	1.0	0.6	0.8

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## SECTION IV

### (U) CONCLUSIONS

Mass spectrometric methods for analysis of solid, liquids and gases related to propellant ingredients and combustion products have been developed.

The spark ion source, used for solids analysis, has been shown to be useful in identifying compounds in combustion products which affect rocket engine combustion performance. Quantitative analysis by spark source technique has been made more accurate by the application of sensitivity values for the elements found in a sample. The sensitivity values can be calculated from available literature data by the equation developed in this task.

Solid propellant ingredients can be analyzed with the spark source for qualitative and quantitative identification of major and minor constituents. All constituents can be identified with one analysis since all ions produced from the sparked sample are integrated on one photoplate spectrum.

This method of analysis also is applicable in determining what effect physical tests have on stability and original chemical concentration of propellant ingredients.

The Knudsen cell source can be used to obtain information on rate and mechanisms of decomposition of solid compounds. Heats of sublimation and vaporization for metals and heats of reaction for solid compounds can be obtained with 7% accuracy using the slope method. The present configuration of the Knudsen cell will not permit thermodynamic studies of compounds which form in high-temperature reactions in the crucible. Pumping rates of the system cannot remove the resultant noncondensable gases rapidly enough, thus causing electrical breakdown to occur from increased pressures in the cell. Auxiliary pumping must be added to the Knudsen cell for further thermodynamic studies of high-temperature reactions.

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Corrosive oxidizers can be studied with the mass spectrometer when all possible reaction sites in the sample introduction system and ion source are eliminated. Use of passivated Monel and Teflon and elimination of construction materials like glass, which react with the corrosive samples, prevents decomposition of the samples by side reaction, thus providing useful analysis of the sample in its original state.



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14. KEY WORDS	LINK A		LINK B		LINK C	
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Knudsen Cell						
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